The PTCR Effect in Donor-doped Barium Titanate: Review of Compositions, Microstructures, Processing and Properties

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Abstract: Barium titanate is widely used in the fabrication of thermistors with a positive temperature coefficient of resistivity (PTCR). The resistivity can increase by several orders of magnitude near the phase transition temperature (T_c) for the ferroelectric tetragonal to the paraelectric cubic phase transformation. There is general agreement that the anomaly in the change of electrical resistivity of donor-doped $BaTiO_3$ around T_c is due to the grain boundary effect. The Heywang-Jonker model and other mechanisms involving the nature of the electrical barrier formed across the grain boundaries of polycrystalline $BaTiO_3$ are reviewed. The compositional effect on $BaTiO_3$-based PTCR properties is listed and discussed. The influences of manufacturing methods under different stages including the initial doping methods, sample forming methods and final heat treatments on PTCR properties are compared. The complex interrelationship between compositions, microstructures, processing and PTCR characteristics are well discussed.

Keywords: *positive temperature coefficient of resistivity (PTCR), barium titanate, composition, microstructure*

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I. Introduction

Positive temperature coefficient of resistivity (PTCR) materials are widely used in the electronics industry for, *inter alia*, applications including temperature sensors, time delay circuits and current limiters for overvoltage or overcurrent protection, overheat protection, current stabilizers. There are four main materials groups in the PTCR family: $BaTiO_3$-based or quasi-$BaTiO_3$-based ternary perovskite compounds,[1-9] ceramic composites,[10, 11] polymer composites,[12, 13] and V_2O_3-based compounds.[14, 15]

$BaTiO_3$ is an insulator at room temperature but donor-doped $BaTiO_3$ with ions such as La^{3+}, Y^{3+}, Sb^{3+}, Nb^{5+} presents semi-conducting behaviour at room temperature and an anomalous increase in resistivity near the ferroelectric-paraelectric Curie transition temperature T_c.[16] This PTCR effect (shown schematically in Figure 1) in barium titanate was first developed in the early 1950s in the Philips Research Laboratories in the Netherlands.[17] Over the past 50 years, diverse applications have triggered research efforts directed toward understanding compositional and structural issues that govern the electrical properties. The screening of dopant candidates from the periodic table has been well scrutinized[18-20] and several models to explain the temperature-resistivity relation have been derived.[21-25]

In the past five decades, there have been few reviews on the PTCR effect in doped barium titanate. Saburi[21] first reviewed semiconducting properties and their relations to the composition of $BaTiO_3$ doped by a variety of donor dopants. He[26] also described and surveyed the processing techniques, fundamental characteristics and applications of PTCR

$BaTiO_3$ ceramics. In a review by Daniels *et al.*[27] the nature of the PTCR effect of donor-doped barium titanate as determined by the conditions of the lattice defects including the oxygen vacancies or/and cation vacancies was described. The thermodynamic and kinetic aspects were discussed. In Nowotny's review,[7] models that have been developed to explain the PTCR phenomenon were compared and discussed. He also listed some materials and processing procedures that could affect PTCR characteristics. In Huybrechts' review,[6] the resistivity-temperature behaviour of PTCR materials by the Heywang-Jonker model was explained. The type and origin of trapped electrons at the grain boundary which cause the PTCR effect were analyzed and the influences on the PTCR effect of changing the processing parameters were presented. Besides those reviews, articles introducing the PTCR effect in $BaTiO_3$ can also be found in several books.[16, 28] However, what is elusive is an explanation of the interrelationships between compositions, microstructures, processing and PTCR properties of donor-doped $BaTiO_3$ materials and a systematic description of all the factors that can influence the PTCR effect. Moreover, there has been tremendous progress in investigating the PTCR effect in barium titanate materials in the last 15 years without a proper review article; a new review in this field is therefore appropriate.

This paper is an attempt to provide a more complete understanding of the interrelationship of compositions, microstructures, processing and PTCR properties. In section II, several mechanisms, including the well-acknowledged Heywang-Jonker model and others which interpret the PTCR effect in donor-doped $BaTiO_3$ are summarized, noting that there is still controversy in terms of the origin of the semiconductivity at room temperature. In the following three sections, the influence on the PTCR effect by altering the composition

(Section III), the processing (IV) and the microstructure (V) are discussed in turn. In the final section, the emerging trends of research of advanced donor-doped $BaTiO_3$ PTCR materials are briefly addressed.

II. Theory

There is a general agreement that the anomaly in the change of electrical resistivity of donor-doped $BaTiO_3$ around T_c is due to the grain boundary effect. No PTCR effect has been observed in $BaTiO_3$ single crystal.[29] Furthermore, it is clear from impedance-plane analysis that the semiconducting characteristics of bulk grains is independent of either temperature or donor concentration.[30-32]

A. The Heywang-Jonker Model

The most accepted model to explain the PTCR behaviour in donor-doped $BaTiO_3$ materials is the Heywang-Jonker model proposed by Heywang[22] and extended by Jonker.[24] Since this model is a fundamental guideline for the understanding of PTCR effect in $BaTiO_3$-based materials, it is necessary to be reviewed again here. There is a bi-dimensional layer of electron traps, i.e. acceptor states, along the grain boundaries of $BaTiO_3$ (shown in Figure 2) exhibiting different electrical properties from those of the bulk phase. The potential barrier ϕ_0 is caused by a two-dimensional electron trap along the grain boundary where acceptor states attract electrons from the bulk resulting in an electron depletion layer with thickness of b. The relation between the density of trapped electrons at the grain boundaries and the

thickness of the depletion layer can be expressed as:

$$b = \frac{N_s}{2N_d} \qquad \text{... ... ... 1}$$

where N_s is the concentration of trapped electrons and N_d is the charge carrier concentration. This depletion layer results in a grain boundary barrier, ϕ_0

$$\phi_0 = \frac{e^2 N_s^2}{8\varepsilon_0 \varepsilon_{gb} N_d} \qquad \text{... ... ... 2}$$

where e is the electron charge, ε_0 the permittivity of free space and ε_{gb} the relative permittivity of the grain boundary region.

The overall resistivity, ρ, is related to the height of the potential barrier by

$$\rho = A\exp\left(\frac{\phi_0}{kT}\right) \qquad \text{... ... ... 3}$$

where A is a geometrical factor and k the Boltzmann constant. Because $BaTiO_3$ is ferroelectric, the dielectric constant, ε, obeys the Curie-Weiss law above its Curie temperature and is given by

$$\varepsilon = \frac{C}{T - T_c} \qquad \text{... ... ... 4}$$

where C is the Curie constant and T the absolute temperature. Incorporating equation (2) and (4) into (3) and rearranging yields:

$$\rho = A\exp\left\{\frac{e^2 N_s^2}{8\varepsilon_0 N_d kC}\left(1 - \frac{T_c}{T}\right)\right\} \qquad \text{... ... ... 5}$$

Above the Curie point when doped $BaTiO_3$ is in the paraelectric phase, the grain-boundary permittivity which follows the Curie-Weiss law decreases with increasing temperature. The corresponding potential barrier increases proportionally and results in steeply increasing resistivity which depends exponentially on the potential barrier as denoted by equation 3.

The energy of the trapped electrons in the grain boundary rises with temperature together with the potential barrier. When the energy of the electron traps reaches the Fermi level, trapped electrons start to jump to the conduction band, which can depress the increase in ϕ_0 and ρ, thus ultimately enhance the conductivity. This also explains the negative temperature coefficient resistivity (NTCR) effect when passing the point ρ_{max} (Figure 1) in the high temperature range.

However, Heywang's model was not able accurately to explain the PTCR behaviour below T_c. Hence Jonker's model[24] was developed as a refinement. Below the Curie point, $BaTiO_3$ is ferroelectric with its polarization along the tetragonal crystal axis. The polarization direction is different from grain to grain because each adjacent grain has a different crystal orientation. Therefore, it creates a net polarization vector (P_N) normal to the grain boundaries, producing surface charges at the grain boundaries which are illustrated in Figure 3. In the areas with negative surface charges, which are around 50% of the grain-boundary area depending on the nature of the ferroelectric material, potential barrier height diminishes or even disappears resulting in the disappearance of the grain boundary resistance. For the other half of the domains containing positive charges, the potential barrier is, of course, getting higher. However, this does not matter as the conducting electrons always follow the path with the lowest barriers so that the material as a whole has low resistivity. This theory is experimentally supported by Huybrechts' work.[33] Furthermore, according to the Heywang-Jonker's model, the electrical resistivity profile $\rho(T)$ above the ferroelectric Curie point of donor-doped barium titanate ceramics can be modelled and was verified successfully using experimentally determined permittivity data

reported by Brzozowski[8] and Zubair[34].

B. Other Theories

In donor-doped $BaTiO_3$ PTCR ceramics, Heywang-Jonker's model has effectively elucidated the change of resistivity with temperature in PTCR characteristics. Based on this model, the PTCR effect increases with increase of potential barrier by which is affected the trapping of electrons (from ionized donors) by acceptor-type species such as some 3-d elements,[35] chemisorbed gases[36-38] or cation vacancies[39, 40] at the grain boundary. Those barriers make the grain boundary more resistive than the bulk grain. However, the model does not fully explain the mechanisms by which electrical properties are influenced adding different amounts or kinds of donor dopants or changing the processing parameters.

It is believed that, for donor-doped $BaTiO_3$, the initial drop in resistivity with increasing donor concentration is generally attributed to an electronic compensation mechanism that induces n-type semiconductor characteristics.[39] Choosing a trivalent ion (R^{3+}) as a donor dopant, free electrons in the $BaTiO_3$ lattice can be generated according to equations (written in Kröger-Vink notation):

$$2O_o^{\times} \Rightarrow O_2 \uparrow +2V_o^{\cdot\cdot} + 4e' \qquad \text{... ... ... 6}$$

and/or

$$R_2O_3 + 2Ba_{Ba}^{\times} \Rightarrow 2R_{Ba}^{\cdot} + 2e' + 2BaO + \frac{1}{2}O_2 \uparrow \qquad \text{……7}$$

Based on equation 6, the free electrons are generated by oxygen deficiency as occurs when sintering at high temperature and/or in reducing atmospheres.[36] Based on equation 7, the

electrons are associated with the replacement of barium ion by R trivalent ion. However, if there is a shift to an ionic compensation mechanism (cation vacancy compensation) at high donor contents, this would result in increasing resistivity at room temperature due to the immobility of cation vacancies. It was first suggested by Jonker and Havinga[40] and the corresponding equation is:

$$2R_2O_3 + 4Ba_{Ba}^{\times} + Ti_{Ti}^{\times} \Rightarrow 4R_{Ba}^{\cdot} + V_{Ti}^{''''} + TiO_2 + 4BaO \qquad \ldots\ldots\ldots 8$$

and/or

$$R_2O_3 + 3Ba_{Ba}^{\times} \Rightarrow 2R_{Ba}^{\cdot} + V_{Ba}^{''} + 3BaO \qquad \ldots\ldots\ldots 9$$

According to equations 8 and 9, barium vacancies and/or titanium vacancies can be produced at the grain boundaries and diffuse from the grain boundaries into the grains during sintering. Because the diffusion speed of cation vacancies is very slow in grains at high temperature, this results in a sample with heterogeneous electric profiles in grains as the cation vacancies act as electron traps and there is an increase in the potential barrier at the grain boundaries. Chan *et at.*[41] inferred that titanium vacancies were favoured defects compared with barium vacancies in the ionic compensation scheme according to a microstructural investigation of highly donor-doped $BaTiO_3$ by TEM. The preference for titanium vacancies is also supported by atomistic simulations which show lower energy of formation than that of barium vacancies.[42]

Smyth[43] believed that equations 7 and 8 can be connected by an exchange reaction:

$$TiO_2 + V_{Ti}^{''''} \Leftrightarrow Ti_{Ti}^{x} + O_2 \uparrow + 4e' \qquad \ldots\ldots\ldots 10$$

where the donor centres are charged-compensated by electrons if the extra oxygen is expelled. Clearly, electron compensation is preferred in reducing conditions during

sintering resulting from the tendency for oxygen loss, while ionic compensation by generated Ti vacancies is favoured by an oxidation environment. This theory explains well the observation that for light donor-doped $BaTiO_3$ material processed in air by slow cooling or annealing at a lower temperature may be superficially or completely oxidized to an insulating state but have low resistance at room temperature if cooled rapidly from the sintering temperature because of the 'frozen-in' composition, avoiding reoxidation that occurs at lower temperature. For higher donor concentrations, materials can become electrical semi-conducting only if sufficiently reduced. The quantitative analysis[44] of the oxygen exchange of donor-doped $BaTiO_3$ both under equilibrium and non-equilibrium conditions by the oxygen coulometry method[45] has directly proved that the carrier concentration is equal to the net donor content which is in agreement with the conclusion that the equilibrium conductivity is dependent on the electronic compensation that is proportional to the donor concentration. Furthermore, evidences for precipitation of secondary phases in donor-doped $BaTiO_3$ when alternated between the oxidizing and reducing environments during firing support the validity of charge compensation mechanism.[46, 47]

There are still some controversies in the well-accepted ideas of changing compensation mechanisms affecting the conductivity of donor-doped $BaTiO_3$. According to the charge compensation theory, the donor-doped $BaTiO_3$ should contain an electrically heterogeneous structure regardless of both the composition and subjecting processing parameters because of the cation-stoichiometric difference between the grain core and grain boundary as compared with the electrically homogeneous structure of undoped $BaTiO_3$. However,

Morrison *et al.*[48, 49] observed by impedance spectroscopy that there is no semiconducting grain interior in lightly donor-doped $BaTiO_3$ after sintered in O_2, which suggested that the material was electrically homogeneous. They also announced that there was no finding of change in cation stoichiometry or precipitation of secondary phase in donor-doped $BaTiO_3$ samples with varied donor concentrations which were sintered in air or argon. Yet it is generally believed that, according to the conventional charge compensation mechanisms, the appearance of a change in cation stoichiometry is required in donor-doped $BaTiO_3$ when a switch from insulating to semiconducting and *vice versa* occurs. They[50] hence proposed an alternative explanation: the oxygen nonstoichiometry, which is dependent on the oxidized/reduced state at the grain boundary is the main reason for the semiconducting behaviour of donor-doped $BaTiO_3$. Furthermore, the production of semiconducting undoped cation-stoichiometric $BaTiO_3$ which exhibits a modest PTCR effect by losing a small amount of oxygen[51] supports their view.

In spite of these discrepancies, there is one common theme that the overall origin of the electrical properties of donor-doped $BaTiO_3$ is a grain boundary effect and greatly influenced by the defect structure on the $BaTiO_3$ perovskite crystal lattice.[52, 53] The proposed grain and grain boundary structure of donor-doped $BaTiO_3$ is schematically displayed in Figure 4.[54] According to the results of measurements of complex-impedance spectra and microstructural analysis by TEM,[54, 55] the grain system's structure is postulated as having three distinct regions (Figure 4(b)) and its equivalent electric circuit model is shown in Figure 4(a). The outer layer is an oxidised, insulating grain boundary region; the intermediate layer is reoxidized, semiconducting outer grain region and the inner layer is an

oxygen deficient grain interior, again, a semiconducting inner grain region. This heterogeneous structure in grains system is supported by both the phenomenon of heterogeneous electric structure of donor-doped $BaTiO_3$ and direct imaging from conductive atomic force microscopy technique.[56, 57]

III. Effect of Composition of $BaTiO_3$-based Materials on the PTCR Properties

Pure $BaTiO_3$ sintered in air is an insulating material at room temperature and no PTCR effect can be observed; however, it turns to a semiconductor at room temperature by doping with various donor dopants such as trivalent ions (e.g. La^{3+}, Sb^{3+}, Y^{3+}) which substitute for the Ba^{2+} site or pentavalent ions (e.g. Sb^{5+}, Nb^{5+}, Ta^{5+}) which substitute for Ti^{4+} site at relatively low doping level. It can revert back to behaving as an insulator when the donor content exceeds the critical concentration (normally less than 1 mol.%) as illustrated in Figure 5,[50] noting that the solubility limits of most of the dopant elements in $BaTiO_3$ perovskite lattices are far higher than this critical concentration.[58] Moreover, the resistivity versus temperature characteristic is very sensitive to the composition of dopants especially for some 3-d elements acting as acceptors. For example, very small additions ranging between 0.01-0.04 mol.% of Mn can increase the PTCR jump of donor-doped $BaTiO_3$ as much as nine orders of magnitude in comparison with three to five orders of magnitudes for donor-doped only $BaTiO_3$.[59] In addition, the additives which play a crucial role in the fabrication of $BaTiO_3$-based PTC thermistors can be mainly distinguished as two kinds: aliovalent dopants and isovalent dopants.

A. Aliovalent Dopants

The effect of the aliovalent dopant on the bulk electrical conductivity is strongly dependent on its substitution site in the $BaTiO_3$ perovskite structure. The type of the incorporated dopant is determined by the difference in valence charge between the dopant and the replaced host ion. Site replacement in the crystal lattice mainly depends on the dopant's ionic radius.[18] Many (3d, 4d and 5d) elements in Table 1 which could act as aliovalent dopants in $BaTiO_3$-based PTC thermistors have been extensively investigated. Among them, the group of rare-earth elements is a rich resource for providing donor dopants.[19, 20, 60, 61]

Three regimes of element (expressed in Table 1) can be identified in terms of site occupancy in $BaTiO_3$ and are summarized as:

i.) For small ions, with ionic radii $r \leq 0.09$ nm, dopants preferentially occupy the Ti-site.

ii.) For intermediate ions, with ionic radii $0.09 \text{ nm} < r < 0.099$ nm, dopants can substitute for either Ti or Ba site depending on dopant concentration, sintering conditions and Ba/Ti molar ratio.[18, 42, 60, 62]

iii.) For larger ions, with ionic radii $r \geq 0.099$ nm, dopants preferentially occupy the Ba-site.

The Ba/Ti ratio of the starting materials seems to play a crucial role in affecting the incorporation of dopant elements into the $BaTiO_3$ lattice. It was observed by electron paramagnetic resonance spectra that Ce^{3+} partially occupied the Ti^{4+} sites when Ba/Ti>1.[63] Electrical conductivity measurement has shown that Er-doped $BaTiO_3$ is weakly semi-

conducting at room temperature when Ba/Ti =1. It behaves as an acceptor (preferential substitution at Ti^{4+} sites) when Ba/Ti >1 but as a donor (preferential substitution at Ba^{2+} sites) when Ba/Ti <1.[18] The recent study of Zhi[64] on $BaTiO_3$ with heavily doped Y^{3+} leads to a similar conclusion. Moreover, dopant substitution at the Ti^{4+} site can also be enhanced by high dopant concentration partly because the solubility at Ti^{4+} sites is higher than that at Ba^{2+} sites.[58] For transition metals, like Mn, Co, Fe and Ni, it is well established that they preferentially substitute for the Ti^{4+} sites regardless the Ba/Ti ratio. Sintering atmosphere likewise has an effect on the preference of the incorporation site of some donor elements such as holmium.[65] Significant substitution of Ho onto Ba sites as a donor occurred in a reducing atmosphere while Ti replacement as an acceptor was preferred when sintered in air.

It is generally observed that the room-temperature resistivity of donor-doped $BaTiO_3$ rapidly increases beyond the critical donor concentration because donor ions are preferentially segregated at the grain boundaries.[31, 66] Desu *et al.*[67, 68] found that at low donor concentration, the donors are compensated electronically, giving a high conductivity. When the donor concentration increases, the donor concentration at the grain boundaries increases even faster due to the segregation until it exceeds a critical level; the compensation mechanism thereafter shifts from electronic compensation to ionic compensation of the donor centre in the grain-boundary region. Hence it creates an insulating layer at the grain boundaries. The total resistivity of the sample can be represented by the grain bulk resistivity and the resistivity from the dopant-segregation-induced insulating region in the grain boundary. The greater the difference in ionic radius between the substitutional dopant and the host ion, the higher is the tendency for such

interfacial segregation to occur. Therefore, the difficulty in preparing semiconducting donor-doped $BaTiO_3$ increases with the radius misfit between the donor and the host ion.[68] Furthermore, Peng[69] and Ting[70] found that when acceptors were added into donor over-doped $BaTiO_3$ insulating material, in which the concentration of donor had exceeded the critical level, the specimen was able to recover some of its semiconducting property. This phenomenon might be explained by assuming that those acceptors inhibit donor segregation at grain boundaries.[71] Nevertheless, the nature of the acceptor states is still little known.

B. Isovalent Dopants

Divalent ions such as Pb^{2+}, Ca^{2+} and Sr^{2+} are extensively used as additives to substitute the Ba ions in the $BaTiO_3$ lattice.[72-76] The replacement by lead can increase the T_c by 4.3°C per percentage atomic replacement, whilst replacement by strontium reduces the T_c by 3.5°C per percentage atomic replacement (shown in Figure 6). Since the Curie temperature for $BaTiO_3$ is 120-130°C, this offers the potential to prepare thermistors with PTCR regions anywhere between -100°C and 250°C. Calcium is frequently used in moderate amount but does not shift the T_c by much, alternatively influencing the grain size of the product.[77] On the other hand, tetravalent ions such as Zr^{4+}, Hf^{4+} and Sn^{4+} have been used as substitutes for Ti ions in the $BaTiO_3$ lattice.[78-80] All those tetravalent dopants substitutions can significantly reduce T_c and readily make the phase transformation of tetragonal-cubic occur at room temperature. Zirconium added to $BaTiO_3$ results in lowering the dielectric loss and broadening the dielectric peak near T_c.[81] Similarly, Hf and Sn exhibit strong ferroelectric-relaxor behaviour at high contents.[82]

IV. Effect of Processing on the PTCR Properties

It is well known that impurities and lattice imperfections play an important role in the exhibition of the PTCR effect in doped-$BaTiO_3$ materials.[83] Their conductivities are considerably influenced by both the intrinsic defects such as oxygen vacancies as well as cation vacancies and the extrinsic defects produced by adding dopants.[69] Furthermore, not only can the equilibrium behaviour of these defects but also the way of defect formation affected by varying sample preparation methods play a crucial role with respect to the semiconducting properties.

A. Effect of Doping Methods

Electrical performance in donor-doped $BaTiO_3$ ceramics is strongly related to the grain structure. Significant differences in microstructure were observed in samples with the same nominal composition prepared by different doping methods even with the same sintering procedures and hereby different PTCR characteristics were exhibited.[84] Hydrothermal synthesis or sol-gel methods can be used to produce donor-doped $BaTiO_3$ systems contained nano-size grains, with high crystallinity and well-dispersed dopants. However, very high room-temperature resistivities and poor PTCR jumps were observed in materials prepared by such method compared with the conventional solid state reaction route.[85-88] A similar phenomenon was observed for donor-doped $BaTiO_3$ prepared by mixing the dopant salt into $BaTiO_3$ powder via solution coating method;[89] in addition, PTCR ceramics prepared by this doping method has lower critical concentration of donor compared with

the same compositional system prepared by the solid state route.[89]

Besides the different doping methods which cause disparities in PTCR behaviour as described above, a variety of unique mixing techniques have been investigated in order to obtain a controllable, microstructurally stable, $BaTiO_3$-based PTCR material. Mukherjee[90] made a donor-doped $BaTiO_3$ system by blending Ba-excess $BaTiO_3$ powder with Ti-excess $BaTiO_3$ powder in different ratios, finding that these blended systems had homogeneous grain size distribution but lower PTCR jumps than those from stoichiometric non-blended batches. Furthermore, Park[91] used a seeding technique to produce a heavily niobium-doped $BaTiO_3$ PTCR material by adding $BaTiO_3$ seed particles which contained double twins produced via preceding heat treatment. Semiconducting and PTCR characteristics were achieved by this seeding method compared with fine grained and insulating material for Nb-doped $BaTiO_3$ at the same doping level produced by a conventional, unseeded route.

Some dopants which are commonly used in making PTC thermistors have high vapour pressure particularly at high temperature so that the possibility of incorporating these dopant ions into the barium titanate crystal lattice by vapour phase diffusion exists. A variety of dopants such as Sb^{3+}, Mn^{2+}, Cd^{2+}, Bi^{3+} and Pb^{2+} have been tested using such methods[92-95] and this resulted in more enhancement of the PTCR jump than doping from conventional solid sources. This is partly because, in diffusion doping from a dopant vapour phase, dopant ions can be more effectively distributed at grain boundaries resulting in increasing the potential barrier at grain boundaries and hence increase of resistivity. In addition, diffusion in polycrystalline $BaTiO_3$ depends on not only the vaporisation rate or

vapour pressure of dopants, but also other factors including the sample's porosity, sample's thickness, the nature of grain boundary and grain size.

B. Effect of Fabrication Methods and Heat Treatment

Not only the various doping techniques, but also the fabrication methods for producing donor-doped $BaTiO_3$ can alter its PTCR performance. In thin-film forming, the electrical properties of the films are significantly different from the bulk, regardless of the techniques of preparation. For Y-doped $BaTiO_3$ thin film (≈2 μm in thickness) deposited by RF-magnetron sputtering as a example,[96] the film has a significant change of PTCR characteristics including a shift to lower T_c and smaller PTCR jump in comparison with the same composition prepared by a solid-state route. Large fluctuations in doping concentration dependent resistivity were also observed among those films themselves with the same composition. Nb-doped $BaTiO_3$ films prepared by laser molecular beam epitaxy (LMBE) show extremely low resistivity (≈10^{-4}-10 Ωcm);[97] films grown by metal-organic chemical vapour deposition (MOCVD) exhibit intermediate resistivity (≈10^{-1}-10^{7} Ωcm);[98, 99] similarly, the resistivity is around 10^{2}-10^{4} Ωcm for films deposited by pulse laser deposition.[100] This phenomenon may be due to the significant change in microstructure and phase content of the deposited thin film compared with its target material. In addition, the evidence that donor element segregates to the surface and the amount of dopant is drastically reduced below the near-surface region of the thin film sample indicates that the ineffective doping is the cause of the contrasted resistivity values for thin film form and bulk sample.[101] $BaTiO_3$-based PTCR ceramics fabricated by thick film methods such as

tape-casting,[102] slip-casting and roll forming[103] have similar microstructure and PTCR characteristics compared with those made by conventional die-pressing methods; nevertheless samples produced by these thick film techniques have higher room-temperature resistivity which is partly due to the high porosity caused by the burning of larger amount of organic additives which were added to facilitate the forming processing.

The PTCR effect in donor-doped $BaTiO_3$ is very sensitive to firing conditions.[104-106] Pure stoichiometric $BaTiO_3$ which is an electrically insulating material at room temperature after sintering in air can become semiconducting and exhibit a PTCR effect when sintered at 1450°C in nitrogen and subsequently quenched.[51] Unlike the segregation of extrinsic defects introduced from foreign dopant elements accommodating in grains and grain boundaries which change the PTCR profiles directly, changing the sintering parameters can change the PTCR characteristics by introducing intrinsic defects such as oxygen vacancies or cation vacancies. Oxygen from the $BaTiO_3$ lattice is gradually lost at high sintering temperature resulted in increasing electrical conductivity; however, the oxygen-deficient material rapidly reoxidizes either on reheating at lower temperatures or on cooling slowly in high oxygen partial pressures. Hence applying reducing atmosphere during sintering can facilitate the conductivity of donor-doped $BaTiO_3$ and enhance the critical donor concentration significantly.[107,108]

The room-temperature resistivity of donor-doped $BaTiO_3$ increases with sintering temperature and dwell time which is attributed to an increase in the amount of acceptor-states along grain boundaries.[109, 110] Kahn[111] and Zubair[112, 113] found that the resistivity of

donor-doped $BaTiO_3$ increases as the rate of cooling is reduced as seen in Figure 7. The authors claimed that this is due to an increase of the activated surface state density in grain boundaries caused by the oxidation during the cooling cycle. However, LaCourse[106] observed that when quenched the Y-doped BT from the sintering temperature, the resistivity below T_c was analogous with that of the sample subjected normal cooling rate as 5°C/min in comparison with the significant lower resistivity exhibited from the sample quenched from 200 °C below the sintering temperature. This is due to the immediately solidified liquid phase staying in the grain boundary increases the thickness of insulating grain boundary layer and hence increases the room-temperature resistivity. The heating rate can also have an influence but has a minor impact on the PTCR characteristics.[114] Liu[115] also observed that an improvement of room-temperature conductivity of lightly donor-doped $BaTiO_3$ can be occurred when a secondary thermal treatment is subjected by reheated the sample to 400~650 °C for 20~40 minutes after firing processing. This is resulted from the relief of internal stress in the crystal lattice through more directional domain alignment thereby reducing the electrical potential barrier. Furthermore, lower room-temperature resistivity of Nb-doped $BaTiO_3$ is obtained by employing a microwave heating technique comparing with conventional sintering in an electric furnace.[116] The mechanism of improvement of PTCR characteristics caused by microwave sintering is still under active investigation.

V. Microstructure-PTCR Property Relationships in Donor-doped $BaTiO_3$

The PTCR behaviour of donor-doped polycrystalline $BaTiO_3$ ceramics is known to be dependent on microstructural aspects such as grain size, domain orientation, phase profile and porosity. It has been generally observed that the room-temperature resistivities (ρ_{RT}) are low for donor-doped $BaTiO_3$ having large grains and the ρ_{RT} of a doped-$BaTiO_3$ sample with fine grains is large (>10^5 Ω·cm).[117] Furthermore, a donor-doped $BaTiO_3$ sample sintered in a non-reducing environment with very fine grains (less than 1 μm) becomes an insulating material and exhibits no PTCR characteristics. The hypotheses that account for large grains in donor-doped $BaTiO_3$ facilitating electric conductivity below T_c are:

i.) As grain boundaries act as insulating layers compared with the internal region of grains, a system with large grains has a lower volume fraction of grain boundaries;[118] this suggests that large grain systems contain relatively lower portions of insulating component on the conducting path in the presence of an applied electric field.

ii.) Based on Daniels' model,[27] the thickness of cation vacancy-rich insulating layers in as-sintered donor-doped $BaTiO_3$ grains can be up to 3 μm. For $BaTiO_3$ samples with fine grains, such cation-vacancy layers which act as acceptor-state dominate the electric structures in grains, resulting in overall insulating profile.

iii.) The high room-temperature resistivity of donor-doped $BaTiO_3$ with small grains can be also accounted for by the strain effect at grain boundaries. The strain which is caused by interfacial segregation of dopants and formation of cation vacancies at grain boundaries increases the potential barrier and hence increases the resistivity.[67] This strain effect becomes more significant for small grain systems and alters its electric properties significantly.

iv.) The mechanism that causes the electrical insulating behaviour of donor-doped

$BaTiO_3$ with nano-sized grains is more complex. There may be a shift of tetragonal-cubic phase transition temperature due to the size effect. Begg *et al.*[119] reported that when the size of $BaTiO_3$ particles is below about 190 nm, the cubic rather than the tetragonal phase is thermodynamically preferred at room temperature. Further investigation by Yashima *et al.*[120] confirmed that the T_c of nano-grained $BaTiO_3$ is suppressed with decreasing particle size and a ferroelectric-paraelectric transition occurs below room temperature leading to disappearance of the PTCR effect above room temperature. Park *et al.*[121] also verified that the crystal phase of the nano-grained $BaTiO_3$ ceramics is a mixed state of the tetragonal and cubic phases. This may well explain the insulating phenomenon at room temperature for donor-doped $BaTiO_3$ made by thin-film processing[122-124] or some sol-gel methods because the $BaTiO_3$ grains are nano-size.

There is a common observation that the grain size of donor-doped $BaTiO_3$ decreases rapidly with increasing donor concentration after exceeding the critical concentration and leading to a rapid increase of resistivity. Desu *et al.* believed, based on Auger electron spectroscopy (AES) results, that this phenomenon is due to the impediment of the boundary mobility caused by interfacial segregation of dopants, including donors and acceptors, at the grain boundaries.[66, 68] As the average donor concentration increases, the excess local concentration of donor at the grain boundary resulting from interfacial segregation would not only retard grain growth but also shift from electronic to ionic compensation, resulting in the formation of highly resistive layers.

Within the same composition, higher PTCR jump (R_{max}/R_{min} ratio) is generally achieved in donor-doped $BaTiO_3$ samples with a heterogeneous grain size distribution and having an optimum porosity, in comparison with materials with large dense grain structures. Kuwabara[125] found that the magnitude of the PTCR jump reaches a maximum at an optimum sintered density (≈75-85% of theoretical density) and then decreases with increasing density. Those results were partially interpreted that the samples with very dense grain structures, i.e. low porosity, indicating containing higher level of conducting-grain to conducting-grain contacts, thus have poor PTCR resistivity jump at T_c.[126] In addition, the enhancement of the PTCR jump by increase of porosity[127, 128] from very dense structure may also be due to the assistance for oxygen transport into the ceramic bulk hence facilitating the oxidation of grain boundaries,[129] which increases the potential barrier and hence the electrical resistivity. However, it is difficult to specify the optimum combination of the grain size and the porosity of as-sintered donor-doped BT sample in order to satisfy both the need for lowering the room-temperature resistivity and increasing PTCR jump.

The domain structure within grains of a donor-doped $BaTiO_3$ can reveal the level of doping. Roseman[126] claimed that an optimal amount of donor can produce unidirectional domain microstructure and domain randomness is only observed in the near grain boundary regions; nevertheless for under-doped and over-doped cases, the domain orientations and widths are random. This phenomenon is suggested to be associated with the Jahn-Teller effect. The spherically asymmetric defect field of optimally donor-doped $BaTiO_3$ can be aligned spontaneously by internal stress generated from Jahn-Teller distortion and this type of defect can, therefore, act as nucleation sites for the ferroelectric phase upon cooling through

the Curie point. However, for under-doped samples, the distorted defect field does not dominate the domain nucleation sources; in case of over-doped $BaTiO_3$ samples, the defect compensation mechanism switches to cation vacancy compensation hence the Jahn-Teller distortion no longer exists. As the electron mobility is anisotropic in the tetragonal unit cell in donor-doped $BaTiO_3$, the aligned domains can facilitate conducting electrons and thus enhance conduction. This can explain why optimal donor-doped $BaTiO_3$ exhibits the lowest resistivity at room temperature.[126]

The PTCR properties are strongly controlled by the microstructural aspects of donor-doped $BaTiO_3$ which is highly sensitive to the cation stoichiometry[90, 117, 130, 131] and processing parameters.[46] Understanding the relationship between microstructure and the PTCR effect and the ways in which microstructure can be changed by chemistry and processing conditions not only help to optimize the performance of PTCR materials but also master potentially the capability for tailoring the PTCR properties by targetedly adjusting composition and processing parameters.

VI. Emerging Trend and Conclusion

After half a century's development, the technologies for fabrication of advanced PTCR thermistors have vastly expanded and improved. The requirements for new PTCR sensors are miniaturization, environmental acceptability and optimizing the PTCR effect by reducing R_{min}, increasing the PTCR jump, decreasing the response time near T_c, increasing T_c and obtaining voltage independence. The single-donor doping system may be inadequate

to satisfy all these needs. Multiple-donor systems are considered as potential solutions. Currently double-donor doping systems including Y_2O_3+Nb_2O_5[132] and Sb_2O_3+Nb_2O_5[133] have been investigated leading to lower room-temperature resistivity. However, the co-influence of the multiple-donor system still remains poorly understood.

Fabrication of multilayer structures of semiconducting $BaTiO_3$ ceramics provides another way to decrease the room-temperature resistivity.[134] This method has the advantage in substantially reducing the room-temperature resistivity over those that rely on change of compositions or heat-treatment parameters because it creates a parallel electric system. However, it is very difficult to co-fire $BaTiO_3$ having PTCR characteristics with an internal electrode system because the need for an oxidizing atmosphere oxidizes base metal electrodes causing severe deterioration to the ohmic contact with the n-type semiconducting $BaTiO_3$.[135] On the other hand, if sintered in a reduced atmosphere, the PTCR effect would be substantially compromised.[38] Therefore, a procedure that prevents oxidation of the internal electrodes without sacrificing the PTCR characteristics during firing is required.

So far, commercially available PTCR thermistors with T_c > 130°C are mainly based on Pb-doped $BaTiO_3$ ceramics. Because of the toxicity of lead oxide and detrimental influence on the environment during the preparation of Pb-contained products, considerately effort is devoted to compositional developments of lead-free PTCR ceramics. Recently, an excellent PTCR effect at 170°C has been reported in the La-doped $95BaTiO_3$-$5(Bi_{0.5}Na_{0.5})TiO_3$ (BT-BNT) ceramics.[136] Furthermore, without adding any foreign donor dopant, a PTCR effect was found in pure BT-BNT solid solution ceramics with low BNT contents.[5, 137] The BT-

BNT system shows PTCR properties comparable to those of lead-containing BT ceramics. However the noncompetitive PTCR jump and strong sensitivity to the oxygen atmosphere during sintering lag its applications. Research is ongoing to tackle those disadvantages.[138, 139] In addition, similar system like $BaTiO_3$-$(Bi_{0.5}K_{0.5})TiO_3$ also attracts many interests most recently.[140-142] Other new systems of lead-free high Curie temperature PTCR ceramics are also demanded.

The PTCR effect in nanograined $BaTiO_3$ ceramics is hardly realized regardless of the compositions or processing parameters. This barrier has limited the application of modern nanotechnologies such as using nanoparticles or thin-film fabrications. Most recently, a few articles have reported that PTCR characteristics could be found in nanograined $BaTiO_3$ ceramics synthesized from surface-coated nanopowders.[121, 143] More work is needed to explore new methods that are able to make very fine grained (≈1 μm) $BaTiO_3$ ceramics exhibiting good PTCR effects which would be a significant step towards creating the next generation miniaturized PTCR devices.

The conventional fabrication methods of PTCR materials are time consuming especially for making different batches having different compositions. Hence high-throughput fabrication of PTCR products in applications to both industrial and research is desire. Currently, a freeforming method of making thick-film PTC thermistor by paste extrusion technology combined with laser sintering is reported.[144] This technique does not require any high temperature post processing as oven-fired is required for PTC ceramics produced by all other methods. This can inspire the new applications of PTCR products in rapid-

prototyping which has never been reported before. The development of PTCR materials is still very often a kind of empirical ("trial and error") science; therefore the high-throughput combinatorial method is a key to the speed-up of production of optimized materials. The London University Search Instrument (LUSI) has been proved the working of the automation system on producing and measuring combinatorial libraries of microwave dielectric ceramics including $Ba_{1-x}Sr_xTiO_3$ (BST)[145] and $Ba_{1-x}Ca_xTiO_3$ (BCT)[146] families. The new study of using such technique on $BaTiO_3$-based PTCR ceramics will be reported and discussed.

In this paper, the state of art in the field of positive temperature coefficient resistivity in $BaTiO_3$-based ceramics is described. Several models to elucidate the PTCR effect in donor-doped $BaTiO_3$ are reviewed. The origin of the room-temperature conductivity of doped-$BaTiO_3$ with PTCR behaviour is due to a combination of multiple mechanisms including the charge compensation scheme and the oxygen-loss theory because neither of them can explain the entire phenomenon individually. The PTCR property of donor-doped $BaTiO_3$ is very sensitive to the chemical composition including the donor's type and concentration, the acceptor's type and concentration, cation stoichiometry and other sintering aid additives. Changing the processing parameters can substantially influence the microstructure and therefore the PTCR performance of donor-doped $BaTiO_3$. There is general agreement that the PTCR behaviour is caused by the grain boundary effect. An understanding of the microstructural aspects of donor-doped $BaTiO_3$ is of fundamental importance for correct interpretation of the PTCR effect. These are materials for which understanding the complex interrelationship between composition and microstructure is necessary to predict and

improve PTCR properties.

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Table Captions

Table 1. Summary of aliovalent dopants in $BaTiO_3$ (ionic radii data from [147]).

Table 1.

Ions	Ionic radius (Å)	Main type of dopant when Ba/Ti=1	Reference
Ba^{2+}	1.35		
Ti^{4+}	0.68		
Sb^{3+}	2.45	Donor	89, 148, 149
Bi^{3+}	1.20	Donor	150
La^{3+}	1.15	Donor	50, 54, 151
Ce^{3+}	1.11	Donor	152, 153
Nd^{3+}	1.08	Donor	68
Sm^{3+}	1.04	Donor	154
Gd^{3+}	1.02	Donor	155
Dy^{3+}	0.99	Donor	156, 157
Ho^{3+}	0.97	Amphoteric dopant	158-161
Er^{3+}	0.96	Amphoteric dopant	162, 163
Y^{3+}	0.93	Amphoteric dopant	64, 164, 165
Yb^{3+}	0.86	Acceptor	2, 18, 166
Ni^{2+}	0.78	Acceptor	167
Cu^{2+}	0.69	Acceptor	168
Cr^{3+}	0.69	Acceptor	59
Mg^{2+}	0.65	Acceptor	71
Fe^{3+}	0.64	Acceptor	169
Co^{3+}	0.63	Acceptor	170
Mn^{2+}	0.80	Acceptor	35, 171, 172
Ta^{5+}	0.73	Donor	150, 173
Nb^{5+}	0.70	Donor	35, 71, 174-176
W^{6+}	0.67	Donor	173
Sb^{5+}	0.62	Donor	4
Mo^{6+}	0.62	Donor	173

Figure Captions.

1. Typical resistivity-temperature characteristic of a $BaTiO_3$-based PTCR material.

2. Electrical double layer at a grain boundary. E_s is the electron-trap energy, E_f the Fermi level, N_s the concentration of trapped electrons and b the width of electron depletion layer.

3. Ferroelectric domains at the grain boundaries. P is the vector of spontaneous polarization and P_N the normal component of P.

4. Schematic model of the microstructure of the donor-doped $BaTiO_3$ and its equivalent electric circuit. (replotted from [54])

5. Schematic representation of the room-temperature dc resistivity as a function of La-dopant concentration for $BaTiO_3$ ceramics sintered in air. (replotted from [50])

6. The effect of isovalent dopant doping on T_c. (replotted from [151])

7. $\rho(T)$ curves as a function of cooling rate for donor-doped $BaTiO_3$ samples. (replotted from [112])

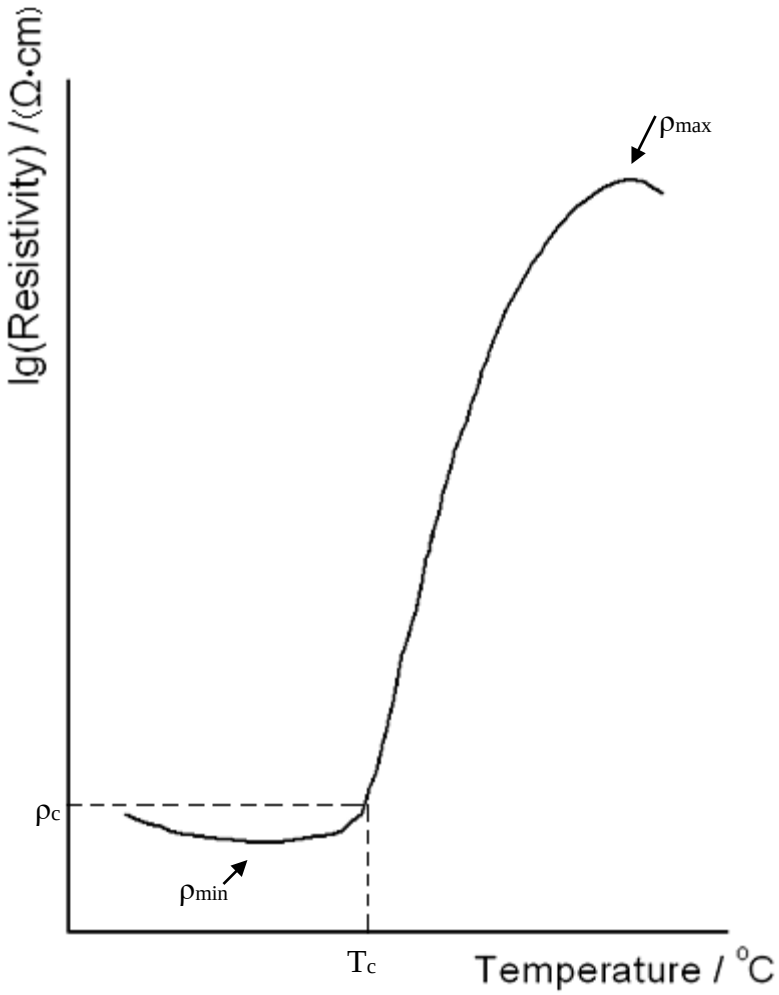

Figure 1.

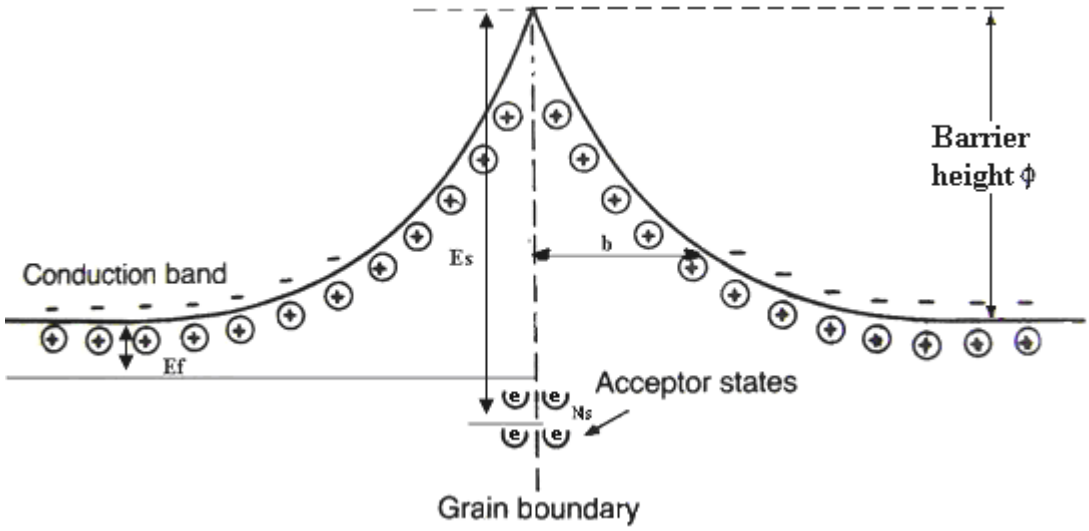

Figure 2.

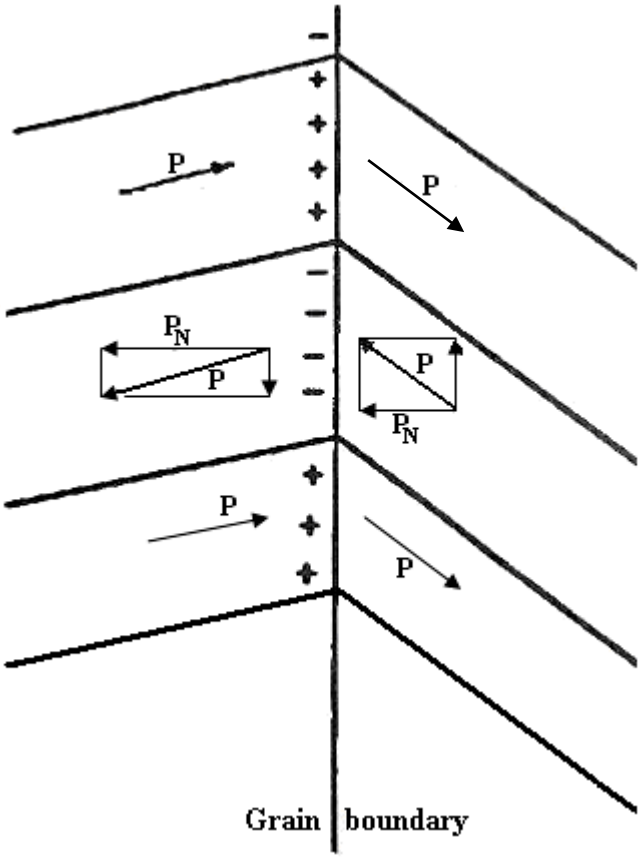

Figure 3.

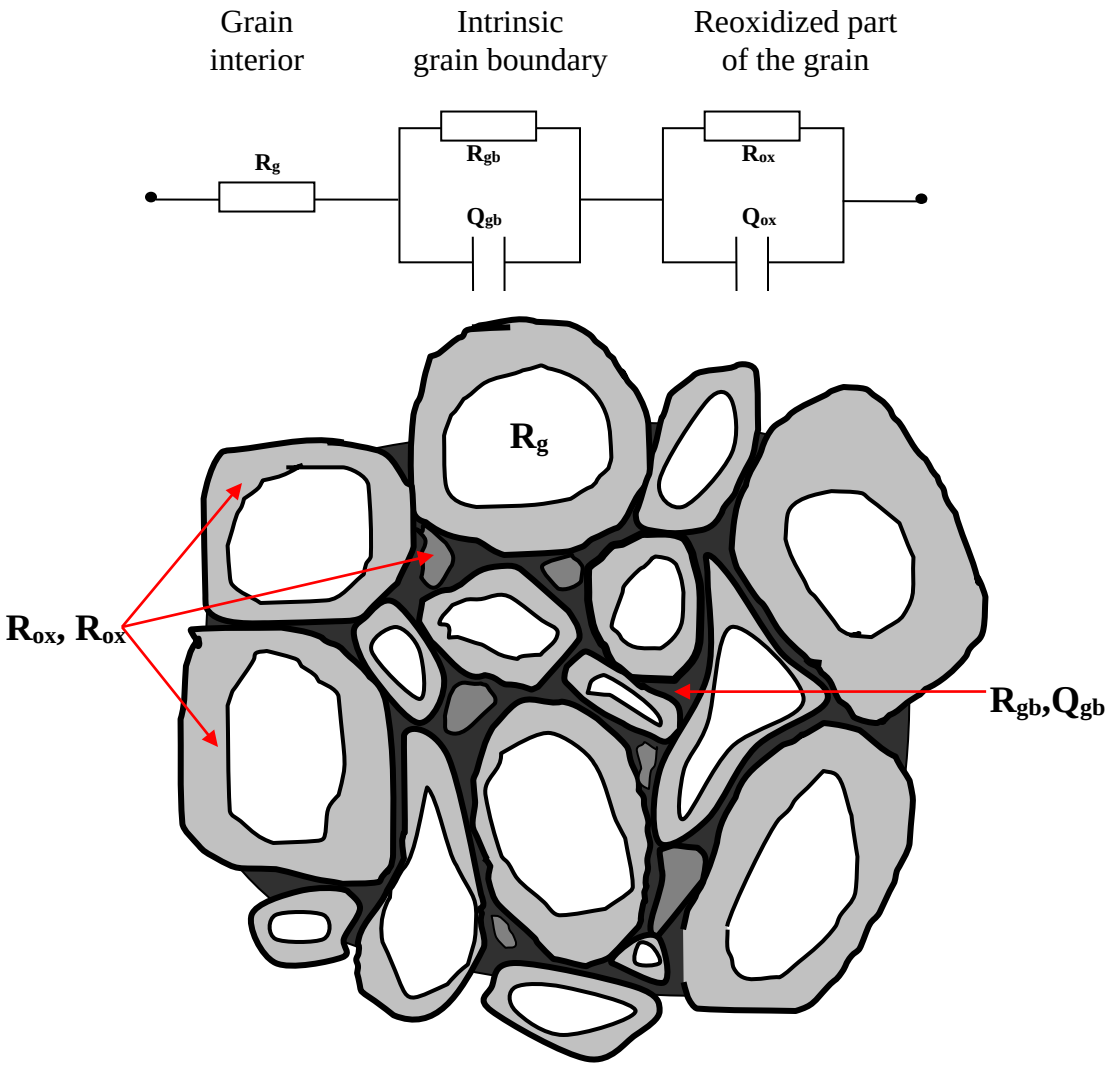
Grain
interior
Intrinsic
grain boundary
Reoxidized part
of the grain
Rg
Rgb
Qgb
Rox
Qox
Rg
Rox, Rox
Rgb,Qgb

Figure 4.

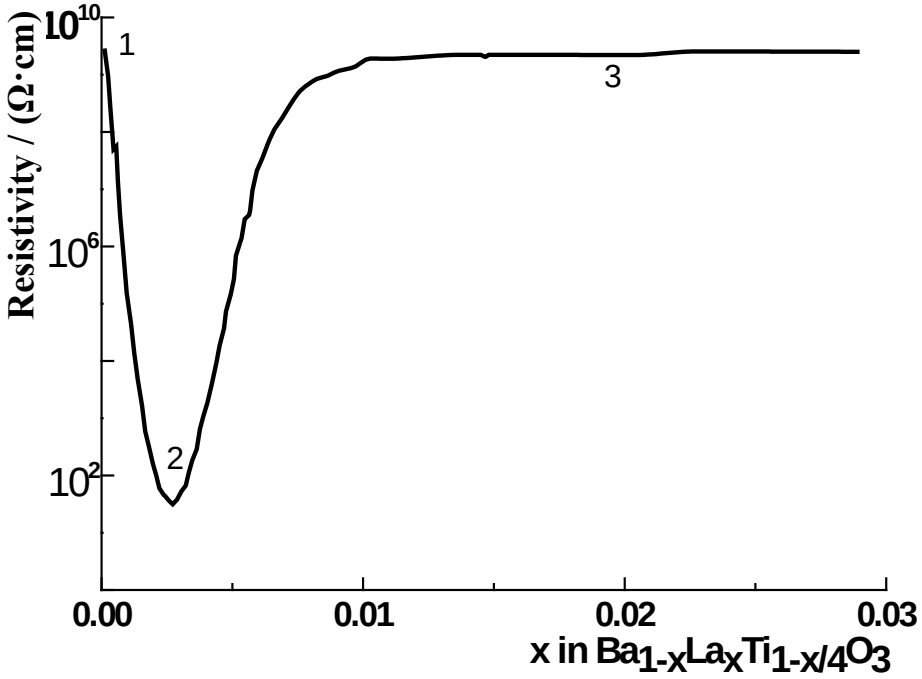
Resistivity / (Ω·cm)
10^10
10^6
10^2
1
2
3
0.00
0.01
0.02
0.03
x in Ba1-xLaxTi1-x/4O3

Figure 5.

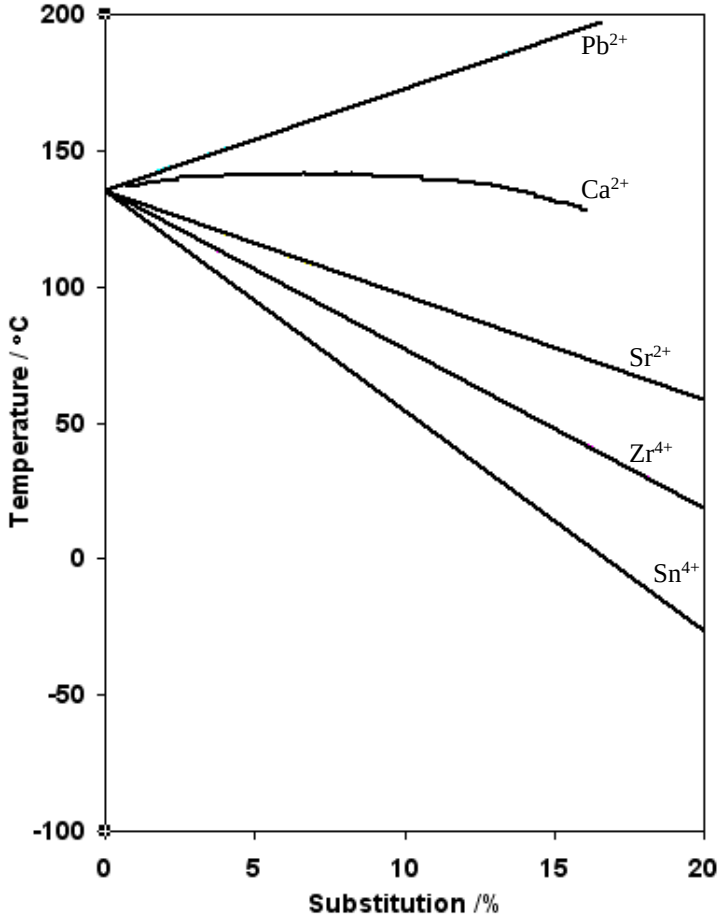
200
150
100
50
0
-50
-100
Temperature / °C
0
5
10
15
20
Substitution /%
Pb2+
Ca2+
Sr2+
Zr4+
Sn4+

Figure 6.

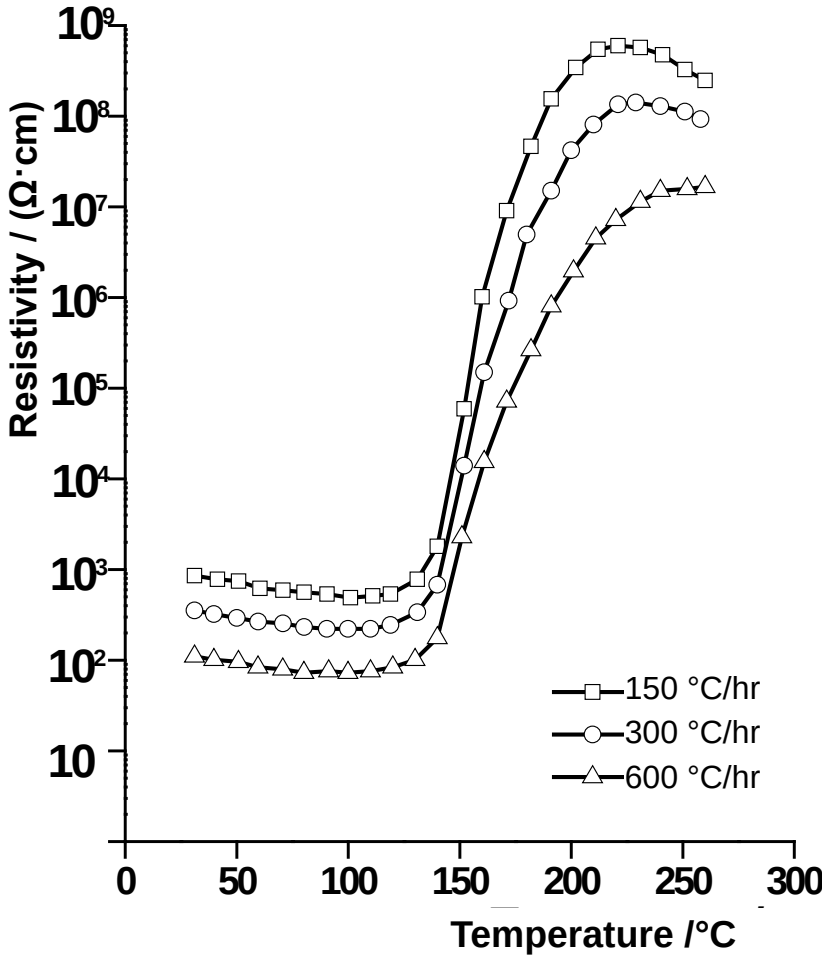
Resistivity / (Ω·cm)
10^9
10^8
10^7
10^6
10^5
10^4
10^3
10^2
10
0
50
100
150
200
250
300
Temperature /°C
150 °C/hr
300 °C/hr
600 °C/hr

Figure 7.